Fingerprinting Crude Oil Resins Using Spectral Stitching HRAM-DIMS

Sundberg, Jonas Folke; Feilberg, Karen L.

Publication date:
2018

Document Version
Publisher's PDF, also known as Version of record

Centre for Oil and Gas - DTU
The Danish Hydrocarbon Research and Technology Centre

Introduction

A detailed knowledge of the molecular composition of crude oil and reservoir fluids is fundamental to understand its formation, physical properties and macroscopic behavior. Our objective is to study compositional changes that occur during recovery processes, and gain a better understanding of the underlying mechanisms on a molecular level. Additionally, parameters that correlates to maturity, biodegradation and oil genetics are employed to understand migration patterns. The results will provide input for computational models that links laboratory-scale enhanced oil recovery (EOR) experiments to theory, and ultimately field applications.

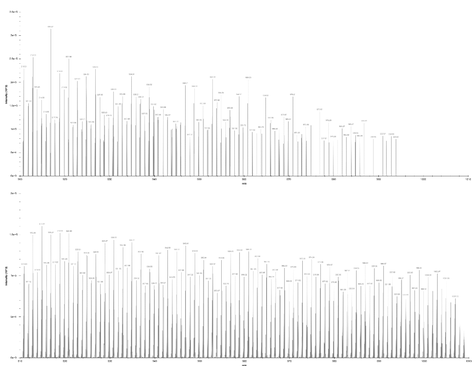
Untangling the Details of North Sea Crude Oil:

Fingerprinting Crude Oil Resins Using Spectral Stitching HRAM-DIMS

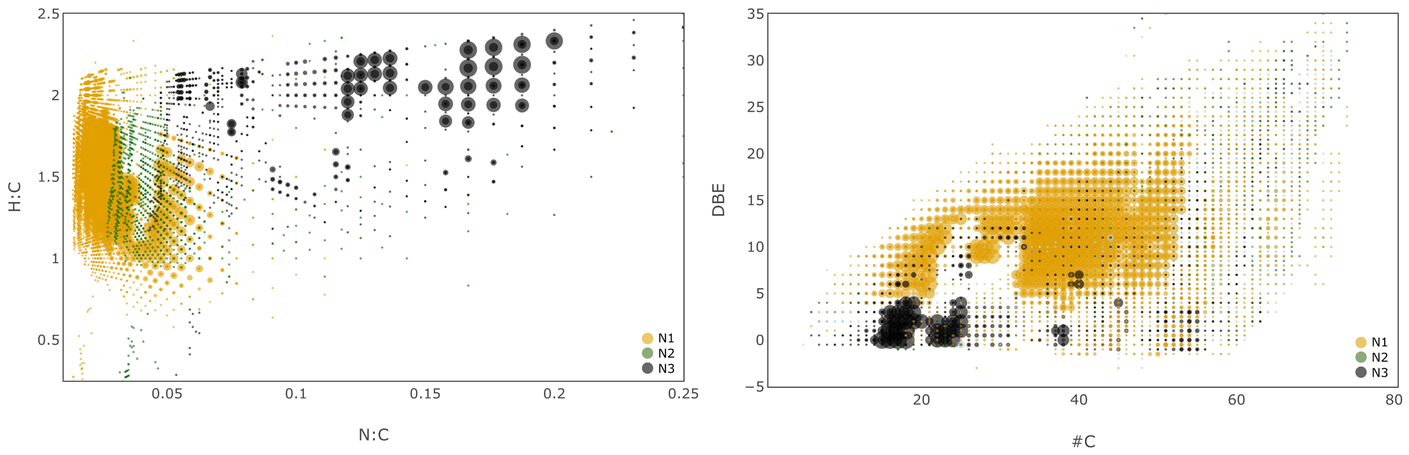
Jonas Sundberg, Karen L. Feilberg

Wide-scan range vs. spectral stitching

Wide-scan range direct infusion mass spectrometry (DIMS) of complex mixtures inherently suffer from discrimination of trace compounds. As an alternative, sequential isolation of small mass-to-charge windows using the quadrupole allows lowering of the ion accumulation in the C-trap of the Q Exactive. This reduces space-charge effects and gives increased mass accuracy, resolution and dynamic range[1]. The SIM-segments are then stitched together to construct a full mass spectra for further analysis. We have observed approximately a three-fold increase in the number of resolved peaks..



WSR (top) vs. spectral stitching (bottom) at *m/z* 900 – 1000.



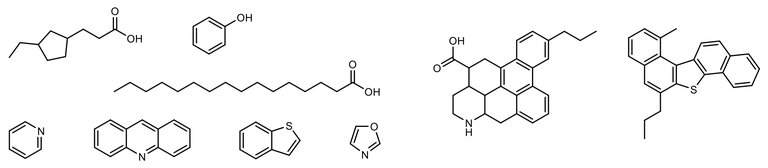
Van Krevelen-diagram and DBE vs. C-plot for a sample from the Danish region of the North Sea.

Compositional space

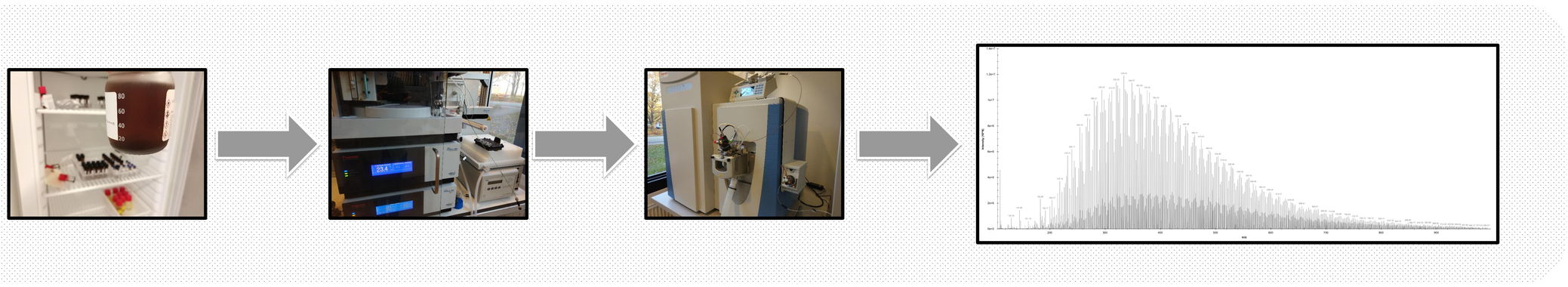
Formula annotations are heavily dependent upon somewhat arbitrary restrictions[4], and prior knowledge of the crude elemental composition is beneficial. The 'Seven golden rules'[3] were adapted with the following elemental restrictions; C<=100, N,S,O<=3 or 6, 1 ppm mass accuracy and where multiple formulations were possible the one with lowest heteroatom content was chosen. As data was collected in positive polarity, a high proportion of the calculated formulas are nitrogen-containing. The majority of species have an H:C ratio of >1 showing the aliphatic character, this is further evident in the DBE versus carbon number plots.

Resins

Oils originating from the Danish part of the North Sea are typically medium gravity with low asphaltene content where the majority of heavy compounds belong to the resins class. Asphaltenes are by definition the fraction of crude oils which is insoluble in light *n*-alkanes, after precipitation of asphaltenes the remaining fraction is called the maltenes which consists of the saturates, aromatics and resins.[2] The latter may then be isolated by for example adsorption on silica or alumina. Compared to asphaltenes, resins typically have higher H:C ratio and contain lower fraction of large condensed aromatic systems. Owing to their polar functionalities, resins are surface active and may alter chalk wettability and thus effect recovery and their characterization is therefore of high importance.



Building blocks of and theoretical molecular structures of resins.

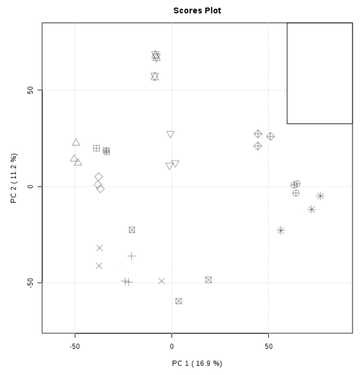


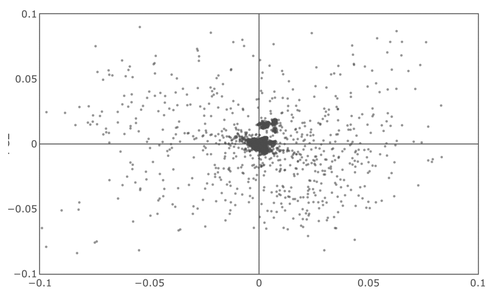
Differential analysis

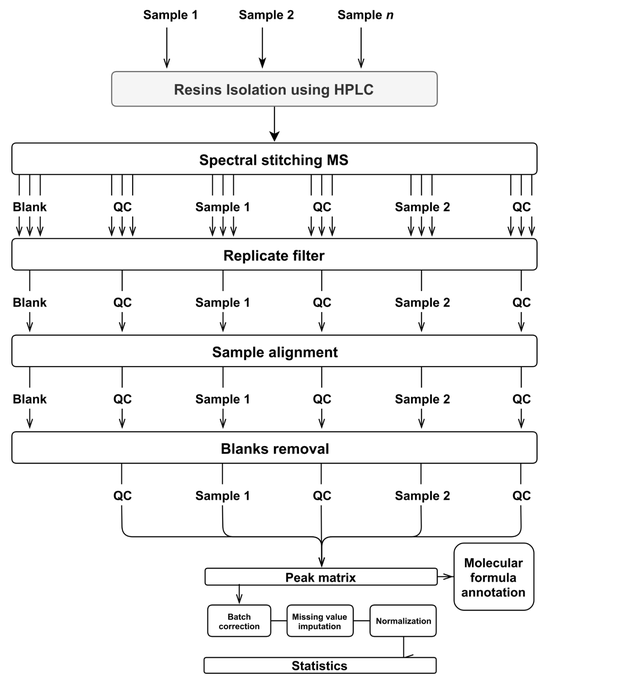
The resins fraction exhibit less susceptibility to weathering and evaporative losses during sample handling, and may therefore be a viable option for oil ‘fingerprinting’ and oil-oil/oil-source correlations. Peak matrices of eleven oil samples were processed for statistical analysis by alignment, missing value imputation (KNN), sum normalization and generalized log transformation. PCA reveals clear well-dependent groupings, demonstrating its usefulness for differentiation of oils. Formula annotation of PCA loadings does not reveal any immediate patterns, and inter-well differences seem to unbe related to specific compound classes. More samples will be characterized for a more thorough study.

Experimental details

Each sample was prepared in three experimental replicates, with each replicate being analyzed in technical triplicates. After asphaltenes precipitation, the resins were isolated using a normal phase HPLC-method as described previously. The collected resin solutions were evaporated to dryness and reconstituted in a mixture of acetonitrile and chloroform containing 0.1% formic acid (v/v). Direct infusion mass spectrometry was carried out on a Q Exactive HF using a HESI-II probe at flow rate 5 µL/min using the following parameters: sheath, aux and sweep gas flow rate 5, 3 and 0 respectively (nitrogen, arbitrary units); capillary temperature, 250 °C; spray voltage, 3.5 kV; S-lens RF level 50, AGC target, 5e5 ; mass-to-charge range, 100−1010 with SIM-segments of 100; resolution, 240 000 at *m/z* 200. Preparation of peak matrices was carried out using the Python-based software DIMSpy[5], briefly as follows; Construction of wide-scan range mass spectra from SIM-segments, replicate filtering (keeping only peaks present in two out of three technical replicates), alignment, blank subtraction and sample filtering (keeping only peaks present in two out of three experimental replicates). Formula annotations were evaluated using three different software based on slightly different approaches; MI-Pack, MFassignR and Formularity[6,7,8]. The data presented herein is based on the latter.







Outlook

Positive mode electrospray ionization is selective for compounds containing protonatable groups, to further study the acidic part of resins we will employ negative mode ionization. Additionally, more comprehensive fractionation will be attempted to reduce the complexity and aid in elucidation of structural features. The workflow will be applied to laboratory scale core-flooding experiments in attempts to understand the influence of resins and polar compounds on recovery processes.

References

1. Southam, A. D., Payne, T. G., Cooper, H. J., Arvanitis, T. N. & Viant, M. R. Anal. Chem. 79, 4595–4602 (2007).
2. Andersen, S. I. & Speight, J. G. Pet. Sci. Technol. 19, 1–34 (2001).
3. Kind, T. & Fiehn, O. BMC Bioinformatics 8, 105 (2007).
4. Koch, B. P., Dittmar, T., Witt, M. & Kattner, G. Anal. Chem. 79, 1758–1763 (2007).
5. https://github.com/computational-metabolomics/dimspy
6. Weber, R. J. M. & Viant, M. RChemom. Intell. Lab. Syst. 104, 75–82 (2010).
7. https://github.com/skschum/MFAssignR
8. Tolić, N. et al. Anal. Chem. 89, 12659–12665 (2017).